MODIFIED MEMBRANES

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A porous polymeric membrane formed from a blend of a polymeric membrane forming material, such as PVDF or polysulfone and a polymeric reactivity modifying agent adapted to modify the surface active properties of the porous polymeric membrane. The reactivity modifying agent is preferably a linear polymeric anhydride, such as poly(alkyl vinyl ether/maleic anhydride). The surface activity modifications include modification of the hydrophilicity/hydrophobicity balance of the membrane, or hydrolysis followed by reaction with a polyamine to form a cross linked polyamide layer. Such modified membranes have use as reverse osmosis membranes.

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(54) Title: MODIFIED MEMBRANES

(57) Abstract: A porous polymeric membrane formed from a blend of a polymeric membrane forming material, such as PVDF or polysulfone and a polymeric reactivity modifying agent adapted to modify the surface active properties of the porous polymeric membrane. The reactivity modifying agent is preferably a linear polymeric anhydride, such as poly(alkyl vinyl ether/maleic anhydride). The surface activity modifications include modification of the hydrophilicity/hydrophobicity balance of the membrane, or hydrolysis followed by reaction with a polyamine to form a cross linked polyamide layer. Such modified membranes have use as reverse osmosis membranes.

5

10   TITLE:

MODIFIED MEMBRANES

TECHNICAL FIELD:

The invention relates to porous membranes which have modified physical

15   properties imparted by the addition of chemical modifiers.

BACKGROUND ART:

Synthetic membranes are used for a variety of applications including

desalination, gas separation, filtration and dialysis. The properties of the membranes

20   vary depending on the morphology of the membrane ie properties such as symmetry,

pore shape and pore size and the polymeric material used to form the membrane.

Different membranes can be used for specific separation processes, including

microfiltration, ultrafiltration and reverse osmosis. Microfiltration and ultrafiltration are

pressure driven processes and are distinguished by the size of the particle or molecule

25   that the membrane is capable of retaining or passing. Microfiltration can remove very

fine colloidal particles in the micrometer and submicrometer range. As a general rule, microfiltration can filter particles down to $0.1\mu m$, whereas ultrafiltration can pass through particles as small as $0.01\mu m$. Reverse Osmosis operates on an even smaller scale.

5   As the size of the particles to be separated increases so too does the pressure required to carry out the separation and the density of the membrane.

A large surface area is needed when a large flux is required. One known technique to make filtration apparatus more compact is to form membranes in the shape of a hollow porous fiber. Modules of such fibres can be made with an extremely large

10   surface area per unit of volume.

Microporous synthetic membranes are particularly suitable for use in hollow fibres and they are produced by phase inversion. In this process, a polymer is dissolved in an appropriate solvent and a suitable viscosity of the solution is achieved. The polymer solution can then be cast as a film or hollow fiber, and then immersed in a

15   precipitation bath such as water. This causes separation of the homogeneous polymer solution into a solid polymer and liquid solvent phase. The precipitated polymer forms a porous structure containing a network of uniform pores. Production parameters that affect the membrane structure and properties include the polymer concentration, the precipitation media and temperature and the amount of solvent and non-solvent in the

20   polymer solution. These factors can be varied to produce microporous membranes with a large range of pore sizes (from less than 0.1 to $20\mu m$), and altering chemical, thermal and mechanical properties.

Microporous phase inversion membranes are particularly well suited to the application of removal of viruses and bacteria. Of all types of membranes, the hollow

25   fiber contains the largest membrane area per unit volume.

Different techniques can be used to induce phase separation and prepare polymer

membranes. A polymer dissolved in a solvent can solidify upon cooling, which is

known as liquid-solid phase separation. Phase separation can be induced either by a

temperature change or by a change in the concentration of the solution. These two

5   processes are referred to as thermally induced phase separation (TIPS) and diffusion

induced phase separation (DIPS). The morphology induced by phase separation needs to

be secured and hence solidification of the polymer phase needs to be achieved. In the

TIPS process this is usually done by dropping the temperature below the glass transition

temperature or the melting point of the polymer. The DIPS process uses a change in

10   concentration, caused by diffusion of a solvent and a non-solvent, to induce a phase

separation. With this technique, the hollow fiber membranes are produced using a

batchwise process. The DIPS process has an advantage that asymmetric membranes can

easily be formed. In addition, the spinning of hollow fibers can be performed at room

temperature, whereas the alternative process – thermally induced phase separation

15   (TIPS) requires much higher temperatures. Since DIPS uses the diffusion of non-solvent

and solvent it is relatively easy to control the rate at which membrane formation takes

place by changing the concentration of the non-solvent bath and the polymer solution.

The disadvantage however, is that macrovoids can be produced, in the form of fingerlike

intrusions in the membrane. They decrease the mechanical strength of the membrane but

20   can be avoided by choosing the right composition of solution.

Flat sheet membranes are prepared in the following way. A polymer solution

consisting of a polymer and solvent is brought into contact with a non-solvent. The

solvent diffuses outwards into the coagulation bath and the non-solvent will diffuse into

the cast film. After a given period of time, the exchange of the non-solvent and solvent

has proceeded such that the solution becomes thermodynamically unstable and demixing

occurs. Finally a flat sheet is obtained with an asymmetric or symmetric structure

Hydrophobic surfaces are defined as "water hating" and hydrophilic surfaces as

"water loving". Many of the polymers that porous membranes are made of are

5   hydrophobic. Water can be forced through a hydrophobic membrane by use of sufficient

pressure, but the pressure needed is very high (150-300 psi), and the membrane may be

damaged at such pressures and generally does not become wetted evenly.

Hydrophobic microporous membranes are characterised by their excellent

chemical resistance, biocompatibility, mechanical strength and separation performance.

10   Thus, in the application of water filtration, such hydrophobic membranes need to be

hydrophilised to allow water to permeate them. Many hydrophilic materials are not

suitable for MF and UF membranes that require mechanical strength and thermal

stability since water molecules play the role of plasticizers.

Currently, poly(tetrafluoroethylene) (PTFE), Polyethylene (PE), Polypropylene

15   (PP) and polyvinylidene fluoride (PVDF) are the most popular and available

hydrophobic membrane materials.   Polyvinylidene fluoride (PVDF) is a semi-

crystalline polymer containing a crystalline phase and an amorphous phase. The

crystalline phase provides good thermal stability whilst the amorphous phase has

· flexibility towards membranes. PVDF, exhibits a number of desirable characteristics for

20   membrane applications, including thermal resistance, chemical resistance (to a range of

corrosive chemicals, including chlorine), and weather (UV) resistance

Modification of a polymer's surface potentially can maintain a polymer's

desirable bulk properties but can provide new, different interfacial properties.

Membranes made from hydrophilic polymers are generally less prone to fouling than the

25   hydrophobic polymers. In some instances, surface modification of the more chemically

resistant polymers has rendered them less susceptible to fouling. Numerous techniques

exist for the surface modification of polymers. The most common examples of this

chemistry are reactions that introduce a single type of functional group or mixture of

functional groups.

5   In general, all techniques of hydrophilisation of polymer surfaces involve an

increase of the surface amount of polar groups. From a microscopic point of view, the

basis of surface hydrophilisation is to maximise hydration and hydrogen bonding

interactions. All sorts of oxygen, nitrogen or sulfur containing organic functional groups

can interact with water more effectively than common carbon based repeating units.

10   There are various methods for wetting a membrane on a non-permanent basis. One

method of hydrophilising a porous hydrophobic membrane has been to pass alcohol

through the pores of the membrane, then replace the alcohol by water. Surfactants and a

post treatment with a glycerol coating have also been used. This is an adequate solution

to the problem, so long as the water remains in the pores. However, if the water is

15   removed from the pores either wholly or partially, and they are filled with air, the

hydrophilised membrane is rendered hydrophobic again, and water cannot pass through

the pores if it is not subjected to high pressure.

          It is an object of the present invention to overcome or ameliorate at least

one of the disadvantages of the prior art, or to provide a useful alternative.

20

DESCRIPTION OF THE INVENTION

According to a first aspect the invention provides a porous polymeric membrane formed from a blend of a polymeric membrane forming material and a polymeric reactivity modifying agent adapted to modify the surface active properties of the porous

5   polymeric membrane relative to a porous polymeric membrane formed from the polymeric membrane forming material alone.

The term "blend" as used herein refers to an intimate mixture or alloy of the polymeric membrane forming material and polymeric reactivity modifying agent which requires that the two components be compatible, ie miscible, with one another.

10   Preferably, the polymeric membrane forming material is of low reactivity relative to the reactivity modifying agent. The polymeric membrane forming material may in some cases desirably be inert.

Preferably, the polymeric membrane forming material is PVDF, especially hydrophobic PVDF.

15   In alternative preferred embodiments, the polymeric membrane forming material is polysulfone. The term polysulfone is used herein in the broad sense in which it is understood by those skilled in the art, and is intended to encompass polysulfone per se, as well as the polyether sulfones, polyaryl sulfones (in particular, polyphenyl sulfone), polyalkyl sulfones, polyaralkyl sulfones and the like.

20   According to a second aspect, the invention provides a method of preparing a porous polymeric membrane wherein the polymeric reactivity modifying agent is blended in the surface active porous polymeric membrane by incorporation into the bulk material

By reactivity modifying agent, it will be understood to include, but not limited to,

25   the overall behaviour of the membrane and/or the membrane surface to chemical species.

In addition to reactivity, the membrane may be modified with respect to other properties. For instance, a particularly preferred reactivity to be modified is the hydrophilicity / hydrophobicity and/or the surface charge of the membrane.

Preferably, the polymeric reactivity modifying agent is a linear polymeric

5   anhydride. Most preferably the polymeric reactivity modifying agent is Gantrez™.

In a first embodiment, the polymeric reactivity modifying agent is included in the surface active porous polymeric membrane by incorporation into the bulk material, for example, by combining with the polymeric membrane forming material prior to or during membrane formation. In particular, the reactivity modifying agent is added to the

10   polymer dope mixture before the membrane is cast.

The reactivity modifying agent may be incorporated into the membrane in a reacted or unreacted form. The reactivity modifying agent incorporated into the polymeric porous membrane may be subjected to chemical modification subsequent to incorporation into the membrane. One preferred chemical modification is hydrolysis to

15   render the membrane hydrophilic. Other preferred chemical modifications include cross linking. In a highly preferred form of the invention, the Gantrez™ is included in the membrane during formation and the resultant Gantrez™ modified membrane is then subjected to crosslinking or an additional treatment which modifies reactivity, such as treatment with one or more of tetraethylenepentamine (TEP), tris- (hydroxymethyl)

20   aminomethane (TRIS), sulfuric acid (H_2SO_4), polyethylene glycol (PEG), calcium carbonate ($CaCO_3$).

Membranes containing reactive surface groups, such as acid or anhydride groups resulting from the incorporation of Gantrez can be crosslinked with crosslinking amines to form amide linkages. The degree of incorporation and extent of crosslinking can be

25   used to construct a membrane suitable for reverse osmosis operations. In this way,

polymeric reactivity modifying agents such as Gantrez can form porous polymeric microfiltration or ultrafiltration membranes which act as substrates for reverse osmosis membranes.

When the polymeric reactivity modifying agent is incorporated into the polymeric
5   membrane forming material before or during membrane formation, it is preferably adapted to combine with the membrane forming material in an amount such that the combined precursor to the surface active porous polymeric membrane acts as a single phase mixture. The membrane may then preferably be prepared by known methods in the art. Most preferably, it is formed into a hollow fibre membrane or a flat sheet
10 membrane.

According to a third aspect, the invention also provides a method of modifying the surface of a porous polymer membrane including:

i) blending a polymeric reactivity modifying agent with a polymeric membrane forming material and

15 ii) forming a modified membrane.

The invention also provides an agent for forming a modified membrane in accordance with the preceding aspects.

According to a fourth aspect the invention provides a blend of a membrane forming polymer and a compatible second polymer, said second polymer
20 being capable of chemical modification after membrane formation.

Preferably, the compatible second polymer is compatible with PVDF, or polysulfone, or more preferably, both.

The commercial copolymer Gantrez™, or poly(methyl vinyl ether/maleic anhydride), is a linear polymeric anhydride which is available in several molecular weight ranges.

Due to the reactive anhydride sites in the Gantrez™ structure and the extensive

5   chemistry associated with this, Gantrez™ can not only provide the appropriate hydrophilicity to the polymer fibers but may provide numerous possibilities for tailoring the fiber to specific applications, depending on the chemistry involved.

In one embodiment of the invention, Gantrez™ was added to the polymer dope mixture and both flat sheet and hollow fiber membranes were produced from this. The

10   primary tests carried out on the flat sheet membranes constituted the initial experimentation, and involved quantifying the dyes absorbed after post-treatment of the membranes.

The hollow fiber membranes produced were tested for tensile strength, permeability, microscopic structure and the change in glass transition temperature of the

15   modified membrane.

Gantrez™ is a commercial ingredient. Its properties and diversity both in the hydrolysed and non-hydrolysed forms are known. Gantrez™ allows membranes to be fabricated which have excess anhydride sites, and by adding various amines and bases for example, the essential mechanical properties of the membranes can be preserved, yet

20   hydrophilicity (and hence flow through the porous membrane) and reaction with other materials can be improved. There can also be a resultant decrease in fouling of the membrane, since say for instance there was a slight negative charge on the fiber then more particles would stay in suspended in solution.

Gantrez™ or poly(methyl vinyl ether/maleic anhydride) is a water soluble copolymer which has the following structure:
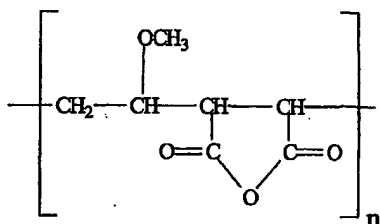
Gantrez™ is a linear polymeric anhydride, which is the interpolymer of methyl

5 vinyl ether and maleic anhydride. Gantrez™ is manufactured by International Specialty Products (ISP) and is available in a range of molecular weights. The physical and chemical properties of some preferred forms of Gantrez™ are listed below:

Appearance: white, fluffy powder

Softening point range $200 - 225°C$

10 Molecular Weights, Specific Viscosity and Glass Transition Temperature:

	M_w	M_N	Viscosity	T_g (°C)
Gantrez™ AN 119	2.13×10^5	6.19×10^4	$0.1 - 0.5$	152
Gantrez™ AN 139	8.72×10^5	2.21×10^5	$1.0 - 1.5$	151
Gantrez™ AN 149	1.25×10^6	3.53×10^5	$1.5 - 2.5$	153
Gantrez™ AN 169	1.89×10^6	5.78×10^5	$2.6 - 3.5$	154

Poly(methyl vinyl ether/maleic anhydride) having a molecular weight in the range 5×10^4 to 5×10^7 may also be used.   The molecular weights were determined by size exclusion chromatography, the specific viscosity carried out at 25°C in a 1% MEK solution in a capillary viscometer.

20   The two monomer types in Gantrez™ individually contribute properties to make the copolymer highly valued material in a variety of applications. The poly(methyl vinyl

ether) is a flexible film former while the maleic anhydride is a hard polar monomer which contributes to bonding strength.

The reaction of maleic anhydride and methyl vinyl ether is as follows:
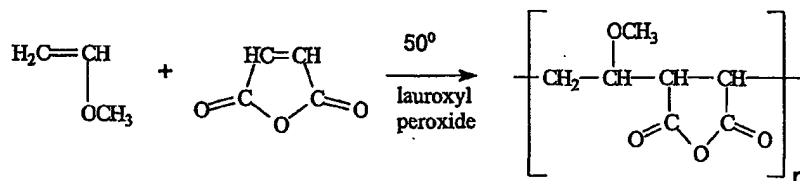
5   Gantrez™ is soluble in water and several organic solvents including alcohols, phenols, pyridine, aldehydes, ketones, lactams and lower aliphatic esters. It is insoluble in aliphatic, aromatic or halogenated hydrocarbons, ethyl ether and nitroparaffins.

When the copolymer dissolves in water or alcohols, the anhydride linkage is cleaved such that the formation of the polar, polymeric free acid or the corresponding

10   partial esters occurs.

Both aqueous and organic solvent solutions of Gantrez™ form films that are tack-free and possess a high tensile and cohesive strength. These films do, however, possess an inherent brittleness, so this property will have to be carefully monitored when incorporating the Gantrez™ into the membrane.

15   Although Gantrez™ powder is hygroscopic and will slowly hydrolyze in a humid environment, it can absorb up to 30wt% water without effecting the flow characteristics of the powder. Mild heating (100°C for 1-2 hours) can remove unbound water.

Several studies have been carried out in making asymmetric membranes using small molecular additives to improve membrane characteristics. Such characteristics

20   include high permeability, good macroscopic integrity such as circular lumen, uniform wall thickness, and mechanical strength. It is known from literature that PVDF has a small critical surface tension (about 25 dynes/cm), the coagulation rate and fiber

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solidification are slow as a result of the weak interaction between the coagulant (water or solvent) and the polymer. As a consequence, difficulties arise when preparing porous asymmetric PVDF hollow fiber membranes without additives.

Surface Grafting in polymer chemistry is a process known in the art by which

5   side chains of a second polymer are introduced onto an existing polymer main chain. Surface grafting generally leads to an overlayer of a second functionalized polymer covalently linked to the substrate polymer. Unlike simple functionalisation, which produces a polymer surface or interphase, grafting produces a physically distinct overlayer with properties that resemble those of the pure graft homopolymer. The

10   methodology for grafting is based on radical polymerisations.

In Contrast to techniques where the surface composition is modified by some external treatment, in bulk modifications the surface composition is the result of the effect of the presence of another component in the polymer system.

The aim for polymer blends is to combine the properties of the single

15   components into one material. By dissolving one polymer in another polymer so that there is an interpenetration of one polymer in another. The "polymer blend" that is synthesized in this way is not stable thermodynamically. Thermodynamic instability means that a demixing process occurs in the melt. To increase the stability it is necessary to crosslink one or both polymers.

20   Surprisingly, it has been found by the present applicants that Gantrez™ is miscible with polar polymers such as the polysulfones and PVDF. Normally, very few polymers are miscible with other polymers - for example, the literature reveals that there is known only one polymer, polyvinyl pyrrolidone (PVP) which is miscible (compatible) with both PVDF and polysulfone.

In the prior art, it is known to use mixtures of two polymeric membrane forming materials which are not miscible. These prior art mixtures require stabilization by cross linking, ie the two non miscible materials are stabilized by chemical reaction, and in this regard, they are not true "blends" as defined herein.

5   Gelation is an important consideration in membrane formation. Gelation can be defined as the formation of a three dimensional network by chemical or physical crosslinking. When gelation occurs, a dilute or more viscous polymer solution is converted into a system of infinite viscosity, that is, a gel. A gel can be considered as a highly elastic, rubberlike solid. It is important to note that gelation is not a phase

10   separation and can occur in a homogeneous solution (that is a polymer and a solvent) as well. Experiments will have to be carefully monitored so as to avoid gelation in the polymer solution, and one of the objectives of the chemical modification of the pre-existing membranes is to optimize the amount of Gantrez™ in the polymer solution without gelation occurring.

15   Gelation of blends which incorporate Gantrez™ can occur if there are multivalent components in the polymer blend such as polyalcohols (in various forms such as sugars, polyvinyl alcohols, polyethylene glycols, ethylene glycol, glycerol and the like). These gelation reactions can be minimized by reducing the time the Gantrez spends in solution with the multivalent components by blending the Gantrez into the membrane forming

20   mixture (or vice versa) immediately prior to membrane casting.

One of the most capable copolymers at binding molecules are maleic anhydride copolymers. The reactions exemplified below are just some of the many reactions that can occur.

As mentioned above, Gantrez™ undergoes hydrolysis quite readily. The

25   hydrolysis reaction was carried out in the presence of a sodium buffer (0.5M sodium

chloride + 0.1M sodium borate pH = 9.3). The problem with hydrolysing the Gantrez™ lies in the fact that the reactive anhydride sites will be lost when this reaction takes place. Secondly, the solvents that Gantrez™ does dissolve in will also dissolve the polymer material that makes the membrane fibers.

5   To overcome this problem, in the surface modification trials, the Gantrez™ is only partially hydrolysed then reacted with the polyfunctional amine, in order to crosslink Gantrez™ with the reactive amine groups. Under the appropriate conditions, the reaction of amine groups can be favoured over hydrolysis even in an aqueous medium.

10   A variety of methods are available for the characterisation of surfaces and permeability. One method to study adsorption or fouling onto a surface is to use radioactive labels, tagged to the appropriate molecule, however this method has proved too cumbersome. Characterisation of the modified membranes is crucial because a small change in one of the membrane production parameters can change the surface structure

15   and consequently have a drastic effect on membrane performance. Structural membrane properties such as pore size and pore size distribution are able to determine which particles or molecules are retained and which will pass through the membrane.

The two techniques primarily used to observe vibrational spectra are infrared (IR) and Raman spectroscopy. The IR spectrum arises from the absorption of radiation,

20   which results from transitions among the various vibrational quantum levels. Infrared testing is carried out primarily on the bulk modified polymer membranes. IR measurements are taken on a polymer solution with and without the Gantrez™ incorporated into the polymer matrix and these two results when compared. One region of interest in the investigation of Gantrez modified polymeric membranes, are the sharp

25   amide peaks around 1700 cm^{-1} wavelength.

Attenuated Total Reflectance, also known as Internal Reflection Spectroscopy is

invaluable in the characterisation of surface layers. This technique relies on the intimate

contact angle of a sample with the surface of a high refractive index, IR-transparent

prism. The basic principles behind this technique is that infrared radiation enters the

5   prism at an angle greater than the critical angle, and is internally reflected at the prism

surfaces, but attenuated by absorptions from the sample contact layer.

Primarily, the SEM is an instrument for the examination of surfaces, and is a very

convenient, simple technique for characterizing and investigating the porous structure of

membranes. The resolution limit of a simple electron microscope lies in the 0.01μm

10   range, with more sophisticated microscopes operating at resolutions of 0.005μm (5nm).

A clear and concise picture of the hollow fiber membrane can be obtained in terms of the

surface and cross-section, and an estimation of the porosity and pore size distribution can

also be obtained.

Many polymers are poor conductors of electricity, and as a result, charge rapidly

15   builds up on the surface of the sample as the electron beam is scanned across it. The

resulting field then interacts with the incident electron beam and causes image distortion.

This problem can be overcome by coating the sample with a conducting layer usually

gold. The gold is applied by sputtering and typical film thicknesses are 20nm.

Sputtering involves creating ions, accelerating them on a target, forming atoms or

20   clusters which are then deposited on the membrane substrate.

The bubble point method is a reflection of the maximum pore size. It is the force

needed to drive a liquid through the pores. The liquid used in this case is water, and the

gas pressure at which a bubble emerges is measured. The maximum pore size can be

calculated from bubble point.

Mechanical tests are often used to assess the ageing or chemical resistance of materials. The change in tensile properties of a material, are useful indicators of the degradation of a material. Testing consists of securing the test sample between two sets of grips. One set of grips is fixed and the other is attached to a moving crosshead and

5   load-cell arrangement. Machines measure the force necessary to elongate and break the sample.

The break force is measured and reported as a tensile stress value by dividing the force obtained by the cross-sectional area:

Tensile stress (Mpa) = F/A

10   Where F = force (Newtons) required to break the test piece, and A = cross-section area of test piece (mm^2). The break force is a reflection of the strength of the polymer fiber and is obviously of high importance in determining performance of the membranes.

Break extension is the elongation measurement from the tensile machine is given by the extension in gauge length divided by the original gauge length. Break Extension

15   is given as a percentage figure, while strain is shown as a fraction.

Tensile strain = change in length/original length = $(l_1 - l_0)l_0$

Where l_1 = length between gauge marks (mm) and l_0 = original gauge length (mm)

Break Extension = $(l_1 - l_0)l_0$ x 100%

The Break Extension is a measure of the elasticity of the polymer fiber, which can also

20   be expressed as Young's modulus or the modulus of elasticity:

Young's modulus = Stress/strain in linear portion of stress-strain curve.

This is the ratio of the applied stress to the strain it produces in the region where strain is proportional to stress. This modulus is primarily a measure of stiffness. Obviously, as the polymer degrades, the break extension will decrease, so these two tests are excellent

25   measures of polymer degradation.

Permeability is a primary factor in governing the performance or efficiency of a

hollow fiber membrane for water filtration applications is the flow or flux through the

membrane. The flux or permeation rate is defined as the volume flowing through the

membrane per unit area and time. The equation that describes the flux is:

5       $J = Q / A \Delta t$

Where Q is the permeated amount, A is the membrane area and Δt the sampling

time. The permeability is an important parameter when considering the effect that the

addition of Gantrez™ has on the membrane performance.

10   BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 shows the time required for complete hydrolysis of Gantrez™ as a function of

temperature.

BEST MODE FOR CARRYING OUT THE INVENTION

15   EXPERIMENTAL METHODS

Production of Flat Sheet Membranes

A dope solution was prepared according to the following formulation :

PVDF	17.1g (17%)
LiCl	3.54g (3.5%)
PVP/VA S630	2.73g (2.7%)
Gantrez	3.09g (3.1%)
NMP	74.3g (73.7%)
	100.76g

20

PVP/VA S630 is polyvinylpyrrolidone/vinyl acetate copolymer

25   NMP is N-methyl pyrrolidone

All ingredients were added together and the dope solution was allowed to mix on

heated rollers (50°C) overnight. Once removed from the rollers, the mixture was left to

settle (to remove any bubbles from the solution) for half a day.

The dope solution was cast onto a glass plate (which was notably hydrophilic)

5   using a glass rod and a membrane was cast by immersing the glass plate into a

precipitation bath consisting of:

    45% PEG-200

    45% H_2O

    10% NMP

10   The membrane was immersed in the precipitation bath for 10 minutes (until the

membrane was able to be "peeled off" the glass plate).

The membrane was divided into equal proportions and samples were soaked in

the following post-treatment solutions until testing was carried out:

    1.   3% Tetra ethylenepentamine (TEP)

15   2.   3% Tris-(hydroxymethyl) aminomethane (TRIS)

    3.   1% Sulfuric Acid (H_2SO_4)

    4.   100% Polyethylene glycol (PEG)

    5.   100% Calcium Carbonate ($CaCO_3$)

    6.   100% Butanol

20   A second flat sheet dope formulation was produced to observe the membrane

without the additive PVP/VA S630. The following solution was made up:

PVDF	17.04g (16.8%)
Gantrez™	3.44g (3.4%)
LiCl	3.88g (3.8%)
NMP	77.02g (76%)

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101.38g

As before, the membrane was cast in a precipitation bath of PEG/H$_2$O/NMP, and

samples immersed in the six solutions mentioned above. The qualitative and

quantitative analysis were carried out as above and results are detailed in the next

5   section.

Analysis of the Flat Sheet Membranes

Both qualitative and quantitative analysis was carried out on the different

membranes. The qualitative analysis that was carried out involved dipping 1cm^2 samples

of membrane into different coloured dyes, namely Saffranin, Methyl Orange and

10   Fuchsin. The intensity of the colours in the membranes was examined visually by taking

photos of the membranes after they had been in the dye solutions for a day. The samples

were then placed in water, and photos were taken of the amount of colour retained and

lost by the membranes. The results are outlined in the next section.

The quantitative analysis involved the measurement of the intensity of the colour

15   retained by the samples using a Hach Spectrophotometer.

Initially, the wavelengths of the dyes had to be calculated using a trial and error

method. Because the region of wavelengths of the colours is known (for example red is

between 500 and 600 nm) the exact wavelength could be calculated. The wavelength

corresponding to the maximum absorbance obtained, was the optimum wavelength of

20   the specific colour.

The calibration for the range of concentrations of colours was then carried out. A

graph of set concentrations versus measured absorbances was plotted. This was

subsequently used to read off the graph unknown concentrations, or to use the calibration

equation to calculate unknown values.

25   Production of Hollow Fiber Membranes

The following dope solutions were used for the production of hollow fiber

membranes: All weights are in grams.

	Dope 1	Dope 2	Dope 3	Dope 4
PVDF	119.3 (17%)	103.76 (17.2%)	102.49 (17%)	102.61 (17%)
Gantrez	21.44 3.1%)	18.43 (3.1%)		18.35 (3.1%)
S630	18.62 2.7%)	16.05 (2.7%)	15.93 (2.65%)	15.66 (2.6%)
LiCl	21.09 (3%)	18.02 (3.0%)	18.32 (3.05%)	18.66 (3.1%)
NMP	520.6 (74.2%)	446.49 (74.1%)	464.6 (77.3%)	446.61 (74.2%)
Total	701.05	602.75	601.34	601.89

The generic brand of PVDF that was used for Dopes 1-3 was Kynar 461, whereas

5   Kynar 500 was used for dope 4, which has a higher molecular weight than Kynar 461.In

the case of Dope 1 was all mixed together on heated rollers for a day and half. Dopes 2-4

were mixed such that the S630

For Dopes 1 to 3 a water precipitation bath (quench) was used. Dope 4 used a

solvent quench which consisted of 45% PEG-200, 45% water and 10% NMP.

10   The following settings were used for production:

	Dope Pump Speed	Lumen Pump Speed	Winder pump speed
Dope 1	150	400	300
Dope 2	350	200	800
Dope 3	350	200	800
Dope 4	250	170	645

For dopes 1 and 4, as soon as the fibers came out of the quench and onto the

winder, they were divided into the six post-treatment solutions outlined below and

immersed until testing took place:

1.   3% Tetra ethylenepentamine (TEP)

2.   3% Tris-(hydroxymethyl) aminomethane (TRIS)

3.   1% Sulfuric Acid (H_2SO_4)

4.   100% Polyethylene glycol (PEG)

5.   100% Calcium Carbonate ($CaCO_3$)

6.   100% Butanol

For dopes 2 and 3, the fibers were left on the winder until production was

complete and then they were divided into the six different post-treatments and one stayed

in the water as a reference.

Dope formulations that were unsuccessful

	Dope 3	Dope 4	Dope 5
PVDF	122.14 (20.3%)	121.49 (20.1%)	100.56 (20%)
Gantrez	18.14 (3%)		15.24 (3%)
S630	15.94 (2.6%)	15.78 (2.6%)	
Sugar			
LiCl	18.65 (3.1%)	19.61 (3.2%)	15.62 (3.1%)
NMP	428.29 (71%)	449.02 (74.1%)	371.2 (73.9%)
Water			
Total	603.16	605.9	502.62

Table ##: Dope formulations that gelled.

Dopes 3, 4 and 5 ingredients were all mixed together on normal rollers over

5   weekend.

Quantitive Results on Flat Sheet Membranes

Using a HACH spectrophotometer, Dope 2 formulation was used and the following

results were obtained :

	Before samples in Methyl orange	After samples in Methyl Orange	Before samples in Saffranin	After samples in Saffranin
TEP	4.5	3.294	3.354	3.159
TRIS	4.5	3.178	3.243	3.131
PEG-200	3.466	3.193	3.243	3.289
CaCO$_3$	4.5	3.275	3.216	2.582
Butanol	3.876	3.178	3.203	3.132
H$_2$SO$_4$	3.165	3.224	3.392	2.943

5 Using Dope 3 formulation, the following results were obtained:

	Before samples in Methyl Orange	After membranes in dye	After membranes in dye with buffer tablet pH7
TEP	0.423	0.219	0.185
TRIS	0.429	0.411	0.367
PEG-200	0.411	0.390	0.350
Butanol	0.429	0.394	0.373
H$_2$SO$_4$	0.440	0.139	0.402
CaCO$_3$	0.427	0.369	0.362

Break Extension results on hollow fibre membranes

The following results are from Dope 1 formulation. All results are expressed as a

percentage break extension by length.

	Wet	Dry
TEP	32.32 ± 7.65	47.20 ± 4.78
TRIS	34.05 ± 7.12	50.13 ± 9.51
PEG	60.51 ± 8.69	33.62 ± 5.55
H_2SO_4	22.57 ± 2.53	21.63 ± 1.56
$CaCO_3$	24.19 ± 8.11	26.30 ± 5.11
Butanol		30.80 ± 6.57

	No Gantrez dope	Gantrez Dope	Kynar 500 Dope
TEP	49.46 ± 9.54	23.64 ± 5.13	58.8 ± 6.13
TRIS	54.46 ± 10.32	17.18 ± 2.308	77.75 ± 10.78
PEG	90.25 ± 11.60	52.75 ± 4.158	123.0 ± 9.1
H_2SO_4	48.28 ± 7.44	6.008 ± 0.868	47.18 ± 13.13
Na_2CO_3	40.55 ± 13.93	18.30 ± 2.41	67.74 ± 9.25
Butanol	60.86 ± 6.60	8.338 ± 3.415	31.48 ± 3.77
Water	44.85 ± 8.79	7.385 ± 2.973	

5

Permeability results on hollow fiber membranes

	Flow time @ 100kPa	Flow time @ 400kPa	# fibers	Length (m)	OD (mm)	LMH @ 100kPa	LMH @ 400kPa
TRIS	39.3	15.0	4	0.6	0.85	143.005	374.672
PEG	36.5	10.4	4	0.6	0.85	153.975	540.393
H$_2$SO$_4$	128.2	33.6	4	0.5	0.85	52.606	200.717
Butanol	116.4	34.3	4	0.4	0.85	72.424	245.776
CaCO$_3$	53.4	14.6	4	0.55	0.85	114.813	419.931

5   LMH - Liter/square meters per hour

	w/o Gantrez	w Gantrez	# fibers	length (m)	OD (µm)	LMH of no Gantrez	LMH of Gantrez
TRIS	127.4	379.3	6	0.45	1000	33.330	11.195
PEG	38.1	965.8	6	0.5	1100	91.187	3.597
H2SO4	95.3	3534.1	6	0.5	1000	40.101	1.081
Butanol	70.7		6	0.5	1000	54.055	
NaCO$_3$	84.7		6	0.55	1000	41.018	
TEP	123.9		6	0.55	1000	28.041	
Water	275.7		6	0.5	1000	13.862	

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1.   A porous polymeric membrane formed from a blend of a polymeric membrane

forming material and a polymeric reactivity modifying agent adapted to modify the

surface active properties of the porous polymeric membrane relative to a porous

polymeric membrane formed from the polymeric membrane forming material alone.

2   A porous polymeric membrane according to claim 1 wherein the polymeric

membrane forming material is PVDF.

3.   A porous polymeric membrane according to claim 1 or claim 2 wherein the

polymeric membrane forming material is hydrophobic PVDF.

4   A porous polymeric membrane according to claim 1 wherein the polymeric

membrane forming material is a polysulfone.

5.   A porous polymeric membrane according to claim 4 wherein the polymeric

membrane forming material is selected from polysulfone, polyether sulfones, polyaryl

sulfones, polyalkyl sulfones and polyaralkyl sulfones.

6.   A porous polymeric membrane according to claim 4 or 5 wherein the polysulfone

is polyphenyl sulfone.

7.   A porous polymeric membrane according to any one of the preceding claims

wherein the reactivity modifying agent modifies the reactivity of the membrane surface

to a chemical species.

8.   A porous polymeric membrane according to any one of the preceding claims

wherein the reactivity modifying agent modifies the hydrophilicity / hydrophobicity

balance of the membrane.

9.   A porous polymeric membrane according to any one of the preceding claims wherein the reactivity modifying agent modifies the surface charge of the membrane.

10.   A porous polymeric membrane according to any one of the preceding claims wherein the reactivity modifying agent is a linear polymeric anhydride.

11.   A porous polymeric membrane according to any one of the preceding claims wherein the reactivity modifying agent is a maleic anhydride copolymer.

12.   A porous polymeric membrane according to any one of the preceding claims wherein the reactivity modifying agent is a poly(alkyl vinyl ether/maleic anhydride).

13.   A porous polymeric membrane according to any one of the preceding claims wherein the reactivity modifying agent is:
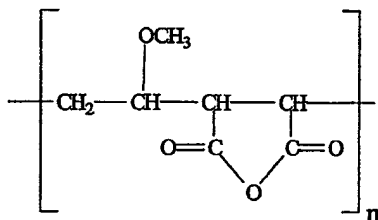
14.   A porous polymeric membrane according to any one of the preceding claims wherein the reactivity modifying agent is poly(methyl vinyl ether/maleic anhydride) of molecular weight 5×10^4 to 5×10^7.

15.   A porous polymeric membrane according to any one of the preceding claims wherein the reactivity modifying agent is poly(methyl vinyl ether/maleic anhydride) of molecular weight 8.72×10^5 to 1.25×10^6.

16.   A porous polymeric membrane according to any one of the preceding claims wherein the reactivity modifying agent is poly(methyl vinyl ether/maleic anhydride) of molecular weight 2.13×10^5 to 1.89×10^6.

17.   A porous polymeric membrane according to any one of the preceding claims including surface anhydride sites.

18.   A porous polymeric membrane according to claim 17 wherein said surface

anhydrides are in reacted form.

19.   A porous polymeric membrane according to claim 18 wherein said surface

anhydrides are reacted with an amine to form an amide linkage.

5   20.   A porous polymeric membrane according to claim 19 wherein said surface

anhydrides are reacted with a polyamine to form a cross linked polyamide layer.

21.   A porous polymeric membrane according to claim 20 wherein said amines are

selected from tetraethylenepentamine (TEP) or tris-(hydroxymethyl) aminomethane

(TRIS).

10   22.   A porous polymeric membrane according to claim 18 wherein said surface active

anhydrides are reacted with an alcohol to form an ester linkage.

23.   A porous polymeric membrane according to claim 22 wherein said surface active

anhydrides is reacted with butanol.

24.   A porous polymeric membrane according to claim 18 wherein said surface

15   anhydrides are reacted with a polyol to form a cross linked polyester layer.

25.   A porous polymeric membrane according to claim 24 wherein said polyol is

polyethylene glycol.

26.   A porous polymeric membrane according to claim 18 wherein said surface

anhydrides are reacted with sulfuric acid.

20   27.   A porous polymeric membrane according to claim 18 wherein said surface

anhydrides are reacted with calcium carbonate.

28.   A porous polymeric membrane according to any one of the preceding claims

wherein there is a negative charge on the surface of the membrane.

29.   A porous polymeric membrane according to any one of the preceding claims

25   wherein the membrane has high permeability.

30.   A porous polymeric membrane according to any one of the preceding claims wherein the membrane has good macroscopic integrity.

31.   A porous polymeric membrane according to any one of the preceding claims wherein the membrane is a hollow fibre.

32.   A porous polymeric membrane according to any one of claims 1 to 30 wherein the membrane is a flat sheet.

33.   A porous polymeric membrane according to any one of the preceding claims wherein the membrane has uniform wall thickness.

34.   A porous polymeric membrane according to any one of the preceding claims wherein the membrane has high mechanical strength.

35.   A method of preparing a porous polymeric membrane wherein the polymeric reactivity modifying agent is blended in the surface active porous polymeric membrane by incorporation into the bulk material.

36.   A method according to claim 35 wherein the polymeric membrane forming material is blended with the polymeric reactivity modifying agent prior to or during membrane formation.

37.   A method according to claim 35 or 36 wherein the reactivity modifying agent is added to the polymeric membrane forming material before the membrane is cast.

38.   A method according to any one of claims 35 to 37 wherein the reactivity modifying agent is added in an unreacted form.

39.   A method according to any one of claims 35 to 37 wherein the reactivity modifying agent is added in a reacted form.

40.   A method according to any one of claims 35 to 39 wherein the reactivity modifying agent incorporated into the polymeric porous membrane is subjected to chemical modification subsequent to incorporation into the membrane.
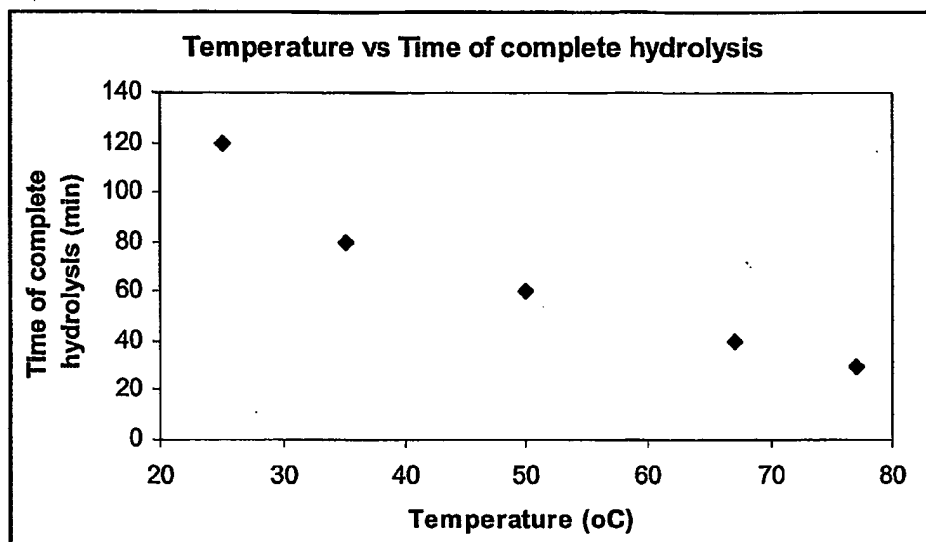
Substitute Sheet
(Rule 26) RO/AU

41.   A method according to any one of claims 35 to 40 wherein the chemical modification is hydrolysis to render the membrane hydrophilic.

42.   A method according to any one of claims 35 to 41 wherein the chemical modification is cross linking.

43.   A method according to any one of claims 35 to 42 wherein the chemical modification is treatment with one or more of tetraethylenepentamine (TEP), tris-(hydroxymethyl) aminomethane (TRIS), sulfuric acid (H₂SO₄), polyethylene glycol (PEG), calcium carbonate (CaCO₃).

44.   A method according to any one of claims 35 to 43 wherein the chemical modification is treatment with crosslinking amines to form amide linkages.

45.   A method of preparing a porous polymeric membrane according to claim 44 wherein the degree of incorporation and extent of crosslinking is selected to construct a membrane suitable for reverse osmosis.

46.   A method according to any one of claims 35 to 45 wherein the polymeric reactivity modifying agent is incorporated into the polymeric membrane forming material before or during membrane formation in an amount such that the combined precursor to the surface active porous polymeric membrane is a single phase mixture.

47.   A method according to any one of claims 35 to 46 wherein the porous polymeric membrane is formed into a hollow fibre membrane.

48.   A method according to any one of claims 35 to 47 wherein the porous polymeric membrane is formed into a flat sheet membrane.

49.   A method according to any one of claims 35 to 48 wherein the porous polymeric membrane is formed from a dope solution including by weight: PVDF 17%; LiCl 3.5%; polyvinylpyrrolidone/vinyl acetate copolymer 2.7%; poly(methyl vinyl ether/maleic anhydride) 3.1%; and N-methyl pyrrolidone 73.7%.

50.   A method according to any one of claims 35 to 48 wherein the porous polymeric

membrane is formed from a dope solution including: PVDF 16.8%; poly(methyl vinyl

ether/maleic anhydride) 3.4%; LiCl 3.8%; and N-Methylpyrrolidone 76%.

51.   A method according to any one of claims 35 to 50 wherein the components are

5   selected such that the melt is thermodynamically stable and no demixing process occurs

in the melt.

52.   A method according to any one of claims 35 to 51 wherein the components and

reaction conditions are selected such that no gelation occurs during membrane casting.

53.   A method according to any one of claims 35 to 52 wherein the dope solution is

10   allowed to mix at about 50°C overnight.

54.   A method according to any one of claims 35 to 53 wherein the dope solution is

formed by the DIPS procedure into a precipitation bath consisting of: PEG-200 45%;

H_2O 45%; and NMP 10%.

55.   A method according to any one of claims 35 to 53 wherein the dope solution is

15   formed by the DIPS procedure into a precipitation bath consisting of water.

56.   A method of modifying the surface of a porous polymer membrane including:

i) blending a polymeric reactivity modifying agent with a polymeric membrane forming

material and

ii) forming a modified membrane.

20   57.   A method according to claim 56 including the step of hydrolysing at least a

surface portion of the polymeric reactivity modifying agent.

58.   A method according to claim 56 or 57 including the step of hydrolysing at least a

surface portion of the polymeric reactivity modifying agent in the presence of a sodium

buffer.

59.   A method according to claim 57 or 58 wherein the surface portion of the

polymeric reactivity modifying agent is only partially hydrolysed.

60.   A method of according to any one of claim 56 to 59 including the step of first at

least partially hydrolysing at least a surface portion of the polymeric reactivity modifying

5   agent then subsequently reacting resultant hydrolysed groups with a polyfunctional

amine.

61.   A method according claim 60 wherein the polyfunctional amine reacts to

crosslink the resultant hydrolysed groups.

62.   A porous polymeric membrane when formed by a method of any one of claims

10   35 to 56.

63.   A porous polymeric membrane according to any one of claims 1 to 34 or when

formed by the method of any one of claims 35 to 56 or modified according to any one of

claims 57 to 61 wherein said polymeric membrane is a reverse osmosis membrane.

64.   A blend of a membrane forming polymer and a compatible second polymer, said

15   second polymer being capable of chemical modification after membrane formation.

65.   A blend according to claim 64 previous wherein said compatible second polymer

is compatible with PVDF.

66.   A blend according to claim 64 wherein said compatible second polymer is

compatible with polysulfone.

20   67.   A blend according to claim 64 wherein said compatible second polymer is

compatible with PVDF and polysulfone.

68.   A blend according to claim 67 wherein said membrane forming polymer is of low

reactivity.

69.   A blend according to claim 68 wherein said membrane forming polymer is inert.

25

FIGURE 1

Temperature vs Time of complete hydrolysis

	International application No.
	PCT/AU01/01450

A.	CLASSIFICATION OF SUBJECT MATTER

Int. Cl. [7]:   B01D 69/02, 71/26, 71/32, 71/34, 71/36, 71/82

According to International Patent Classification (IPC) or to both national classification and IPC

B.	FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
B01D 69/02, 13/00, 71/26, 71/32, 71/34, 71/36, 71/82

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
AU: IPC AS ABOVE

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
Derwent WPAT

C.	DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 99/59707 A (USF FILTRATION AND SEPARATIONS GROUP, INC.) 25 November 1999 See page 8 lines 6-21	1-3,8,9,29-34,63
X	Derwent Abstract Accession No. 86-343157/52, JP 61257203 A (TERUMO CORP) 14 November 1986	1-3,8,9,29-34,63
X	Derwent Abstract Accession No. 87-357035/51, EP 250337 A (RHONE-POULENC RECH) 23 December 1987	1-3,8,9,29-34,63

X	Further documents are listed in the continuation of Box C	X	See patent family annex

Date of the actual completion of the international search	Date of mailing of the international search report
29 November 2001	~3 DEC 2001
Name and mailing address of the ISA/AU	Authorized officer
AUSTRALIAN PATENT OFFICE PO BOX 200, WODEN ACT 2606, AUSTRALIA E-mail address: pct@ipaustralia.gov.au Facsimile No. (02) 6285 3929	MATTHEW FRANCIS Telephone No : (02) 6283 2424

C (Continuation).   DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	Derwent Abstract Accession No. 90-255073/34, DE 3904544 A (FRAUNHOFER-GES FORD ANGE) 16 August 1990	1-3,8,9,29-34,63
X	Derwent Abstract Accession No. 91-016142/03, EP 407900 A (AKZO NV) 16 January 1991	1-3,8,9,29-34,63
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X ·	Derwent Abstract Accession No. 93-079595/10, JP 05023557 A (ASAHI CHEM IND CO LTD) 2 February 1993	1-3,8,9,29-34,63
X	WO 99/01207 A (ZENON ENVIRONMENTAL INC.) 14 January 1999 See abstract	1-3,8,9,29-34,63
X	Derwent Abstract Accession No. 88-157862/23, JP 63097634 A (TORAY IND INC) 28 April 1988	1-5,8,9,29-34,63
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X	Derwent Abstract Accession No. 89-139655/19, FR 2620712 A (PENNWALT CORP) 24 March 1989	1-3,8,9,29-34,63
A	Derwent Abstract Accession No. 83-702144/27, JP 58088007 A (ASAHI GLASS KK) 26 May 1983	

		International application No.
		PCT/AU01/01450

C (Continuation)	DOCUMENTS CONSIDERED TO BE RELEVANT	
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 50447 B1 (ASAHI GLASS COMPANY LTD) 2 October 1985	
X	US 5531900 A (RAGHAVAN ET AL) 2 July 1996	1-3,8,9,29-34,63
A	Derwent Abstract Accession No. 87-260133/37, JP 62179540 A (ASAHI CHEMICAL IND KK) 6 August 1987	

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

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EP	250337	FR	2600265	US	4810384				
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EP	430082	JP	3186325	US	5079272	US	5158721		
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		DD	296221						
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JP	5023557	NONE							
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JP	63097634	NONE							
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EP	911073	AU	88378/98	JP	11188247	US	6083393		
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US	5531900	NONE							
JP	62179540	NONE							

END OF ANNEX